

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

(10) International Publication Number
WO 01/22133 A1

- (51) International Patent Classification⁷: **G02B 6/12**, C08L 63/00 (74) Agent: **ELLIS-JONES, Patrick, George, Armine; J.A. Kemp & Co.**, 14 South Square, Gray's Inn, London WC1R 5LX (GB).
- (21) International Application Number: PCT/GB00/03603
- (22) International Filing Date:
20 September 2000 (20.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
9922196.2 20 September 1999 (20.09.1999) GB
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (71) Applicant (*for all designated States except US*): **ISIS INNOVATION LIMITED** [GB/GB]; Ewert House, Ewert Place, Summertown, Oxford OX2 7BZ (GB).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **TURBERFIELD, Andrew, Jonathan** [GB/GB]; 29 Derwent Avenue, Headington, Oxfordshire OX3 0AR (GB). **DENNING, Robert, Gordon** [GB/GB]; 26 The Row, Toothaldon, Oxfordshire OX44 9NE (GB).
- Published:
— *With international search report.*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 01/22133 A1

(54) Title: **PHOTONIC CRYSTAL MATERIALS**

(57) Abstract: A method of forming a photonic crystal material is disclosed comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3, with an equivalent weight per crosslinkable group of at most 1000, e.g. a glycidyl ether of bisphenol A novolac resin, preferably a SU-8 negative photoresist.

PHOTONIC CRYSTAL MATERIALS

5 This invention relates to photonic crystal materials and a method for their preparation.

10 In our WO99/09439 we describe a photonic crystal material that has a 3-D periodic structure with a periodicity that varies on a length scale comparable to the wavelength of electromagnetic radiation. The 3-D periodic structure is produced by irradiating photosensitive material with electromagnetic radiation such that interference between radiation propagating in different directions within the sample gives rise to a 3-D periodic variation in intensity within the sample. Thereafter the irradiated material is developed to remove the less or more irradiated regions of the material to produce a structure having 3-D periodicity in the refractive index of the composite material (because irradiation produces a change in the refractive index). In general, the less irradiated regions are subsequently removed leaving voids which can, if desired, be filled, for example with material having a refractive index which is different from that of the irradiated photosensitive material. If desired, the irradiated sample can be used as a template for the production of other materials having periodic variations in refractive index.

25 The present invention relates to an improved process for the production of such photonic crystal materials.

30 In particular, it has now been found that improved results can be obtained by using a photosensitive material with a high degree of functionality. According to the present invention there is provided a method forming a photonic crystal material comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the

photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3 or 3.5 with an equivalent weight per crosslinkable group of at most 1000. It has been found that with high functionality the network of crosslinks formed is potentially very dense giving high solubility contrast between strongly and weakly exposed material.

In general the photosensitive materials used in this invention are those possessing an average number of crosslinkable groups per molecule of at least 4, preferably at least 6 and especially about 8. They have an equivalent weight per crosslinkable group (XEW) in general at most 500, typically at most 400, preferably at most 300, especially at most 230. Suitable photosensitive materials which can be used include epoxy resins ie. epoxy groups act as the crosslinkable groups.

It has been found that it is particularly advantageous to use the glycidyl ether of bisphenol A novolac which is available as EPON-SU-8 from Shell Chemicals. This resin has low intrinsic absorption at the laser wavelength ($\lambda = 355$ nm) and is capable of sub-0.1 micron resolution. It has an average of 8 epoxy groups per molecule. The material is therefore mostly in the form of a tetramer although other oligomers will usually be present. Its XEW is generally about 215, with a typical range from 190 to 230. It may be desirable to co-polymerise this material with a less crosslinkable plasticising epoxy monomer e.g. one with a single epoxy group in order to minimise shrinkage and/or film distortion on heating of the material (thereby reducing the functionality somewhat). Alternatively, the resin can be modified by using a so-called "expanding" monomer such as a spiro-orthocarbonate. Alternatively, improved physical properties of the polymer can be obtained by the addition of a binding agent such as a linear polymer. Effectively, any polymer can be used provided that it has sufficiently high functionality and the precursors have a low degree of optical absorption at the laser wavelength within a film typically 10-100 microns thick.

In one preferred embodiment of the present invention the photosensitive material is subjected to irradiation in the presence of a photoacid generator. Subsequent to exposure the material is heated to cure the crosslinked material.

5 Suitable photoacid generators (PAG) which can be used, especially with epoxy resins, include onium salts such as triaryl sulfonium salts including triphenyl sulfonium antimony chloride which is available as Cyracure UV1 from Union Carbide. This particular generator is well suited to irradiation at 355 nm where it has sufficient absorption

10 (molar extinction coefficient $\sim 300 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). In general the molar extinction coefficient of the PAG should be from $50 - 2000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at the laser wavelength. If the molecular coefficient is too large, the requirement for the sample to be optically thin means that the concentration of initiators is too small to effect polymerisation. On the other hand if it is too small, the PAG

15 concentration is so high that it adversely affects the properties of the polymer. By "optically thin" is meant that at the concentration at which it is used the PAG does not absorb more than 5% of the radiation which is incident upon it. In addition the quantum efficiency of the PAG should be sufficient for the exposure to cause insolubilisation of the photosensitive material. The effective quantum

20 efficiency will be enhanced if the system involves chemical amplification. Obviously sufficient photosensitive material must be insolubilised to provide a volume of insolubilised material which is useful for practical purposes i.e. a useful volume, for example 1 mm^3 e.g. a film of size $5 \times 5 \times 0.04 \text{ mm}$. By "cause insolubilisation" is meant that there is sufficient proton generation for subsequent

25 acid catalysed polymerisation, as discussed below, to result in a crosslinked material which is insoluble in a solvent which dissolves the unirradiated or weakly irradiated material. One of skill in the art will, of course, be able to select an appropriate PAG from those possessing the required molar extinction coefficients and optical thinness. For SU-8 a quantum efficiency of about 0.2 is needed for

30 proton generation in the PAG. It is believed that the insolubility threshold is reached when each absorbed photon leads to the conversion of material equivalent

to about 250 or 500 crosslinkable groups, for example about 600 epoxy groups, into insoluble polymer.

5 It will be appreciated that if a photonic crystal is to be prepared using a different wavelength source then a different PAG will generally be needed. One of skill in the art will be able to select an appropriate PAG given the literature on this subject for microlithography. Alternatively, the addition of a sensitizer which is not in itself absorbing generally renders the PAG effective for longer wavelengths. For shorter wavelengths other triaryl sulfonium salts or diaryl-iodonium salts can
10 generally be used.

It is a further feature of the present invention that the subsequent curing or baking of the exposed material is carried out at a temperature below the melting of the precursor in order to suppress proton diffusion and thus maintain a fidelity
15 with the intensity pattern. This contrasts with the conditions used in conventional lithography for semi-conductor fabrication. It will be appreciated that the exposure to light results in the production of a proton from the photochemically induced fragmentation of the PAG molecule. Acid catalysed polymerisation of the resin occurs at the post-exposure bake. The precise
20 temperature and time will depend on the exposure dose, the concentration of PAG in the resist and the required filling factor. Typically, though, the bake will take place at 40 to 120°C for, say, 1 to 20 minutes. Since the melting point of the SU-8 resin is 80 to 90°C, the temperature should be kept below this in order that a much "cleaner" lattice is produced.
25 In effect, therefore, exposure produces a latent image which is realised on subsequent baking. In view of this latency it is possible to employ multiple exposures, well separated in time. This can be used, for example, to superimpose two different periodicities or to write specific defect or waveguide structures into the material, before or after the principal exposure.

30

In order to prepare a film of the photoresist material, it is first dissolved in

a suitable solvent. The solution is typically spun onto a fused silica disk. Alternatively the film can be prepared by, for example, spreading, moulding or pouring. For EPON-SU-8 a suitable solvent is γ -butyrolactone, typically at 50 to 60% weight resist concentration, which can be obtained with gentle heating (~30 to 40°C) and manual stirring, with the resulting viscous solution filtered to exclude particles larger than, say 1 μ m. Typically the 50% weight resist can be used to give rise to a film from 2 to 30 microns thick while the 60% material will give a thickness of 10 to 60 microns. The solution also contains the PAG, typically at a concentration of 0.5 to 3%, generally from 1.0 to 2.0%, by weight. The amount of PAG added determines the sensitivity; with this particular combination about 1.2% concentration gives good results. The photosensitive material can be stored in the dark away from the heat sources until required.

Approximately 2 ml of the solution can be pipetted onto a disk, typically of fused silica, of about 2 cm diameter so that it is flooded, to prepare a film of about 30 μ m. The film is then spun at, typically 1000 rpm (5s ramp up, 40s hold, 5s ramp down). The material is then heated to evaporate the solvent, typically at 50°C for 5 minutes and followed by 15 minutes at 90-100°C. The interval between film preparation and exposure should be kept as short as possible and generally less than 30 minutes.

The film is then exposed to an interference pattern created at the intersection of four beams from a frequency-tripled, injection seeded, Q-switched Nd:Yag laser (wavelength $\lambda=355$ nm). Such a pattern has three-dimensional translational symmetry.

The propagation directions, polarisation directions and relative intensities used are defined as follows

Normalised optical wave-vectors, relative to the conventional fcc unit cells axes:

- 6 -

(0)	-0.57735027	-0.57735027	-0.57735027
(1)	-0.96225038	-0.19245008	-0.19245008
(2)	-0.19245008	-0.99225038	-0.19245008
(3)	-0.19245008	-0.19245008	-0.96225038

5

Polarization unit vectors in the same frame,

(0)	-0.812024	0.332099	0.479924
(1)	0.269517	-0.575382	-0.772202
(2)	0.804841	-0.0425761	-0.591961
(3)	0.933817	-0.337270	-0.119310

10

Relative intensities ($I_0:I_1:I_2:I_3$); (7:1:1:1)

The films were exposed in a single pulse (6 ns) of the laser. The total dose can be varied from 80-200mJcm⁻² depending on the required polymer/air ratio in the photonic crystal. (The filling factor is also related to the time and temperature of the post exposure bake). The glass substrate was index matched to a thick glass block using mineral oil in order to reduce back reflections.

15

The beam geometries described above are those required to define the appropriate interference pattern in air. In practice refraction occurs as the beam enters the film of resist but it is possible to compensate for the refraction by changing the angle of the beams. This can be done, for example, by adding a shaped transparent optical element or elements with refractive index greater than unity into the beam paths, and may include the use of high index liquid between rigid optical elements.

25

The pulse duration is not critical. With an injection seeded laser the coherence length is equal to the pulse length, but this requirement can be relaxed if the optical path-lengths are made accurately equal. A cheaper but less effective option for increasing the coherence length is etalon-narrowing. In practice it is only necessary to achieve a coherence length of ~1cm. An ordinary un-narrowed

30

Q-Switched Nd-YAG laser can approach this requirement. More importantly though injection-seeding makes the pulse energies, following third harmonic generation, far more reproducible, so that the control of the dose in a single pulse exposure becomes straightforward. Typically electromagnetic radiation is directed
5 at the sample from at least four beams so as to intersect and interfere within it.

Alternative lasers can be used, providing the photo initiator is chosen to match the operating wavelength. An optical parametric oscillator which is continuously tunable, could therefore be used to construct crystals with different
10 interference patterns with or without a change in the angles between the interfering beams. The main advantage of single pulse operation is the absence of significant refractive index changes, that could perturb the interference, during the exposure.

After exposure the film is baked to cure the resin. This can be achieved by
15 placing the glass substrate on a level hotplate at 40-120°C for 1-20 minutes. The film is then developed to dissolve away the uncrosslinked resin. For the epoxy resin SU-8 this can be achieved by using propyl glycol methyl ether acetate (PGMEA). Typically the substrate with the attached film is placed in a container
20 with the solvent in an ultrasonic bath until the film becomes detached. The power is damped or attenuated to ~7W to avoid mechanical damage to the film as it releases from the substrate. Typically this is achieved at a temperature of 40 to 50°C for, say, 40 minutes for a 30 micron film. After this the film is washed with fresh PGMEA and then rinsed before drying. For this purpose an alcohol such as
25 isopropyl alcohol can be used. In this way we have prepared photonic crystal films with thicknesses from 10 to 80 μm (e.g. 10 to 30 μm), corresponding to 14 to 84 (e.g. 14 to 42) close-packed layers.

All other features of the method described in WO99/09439, to which
30 reference should be made, can be used. For example the photosensitive material can be subjected to multiple exposures, each exposure producing respective

interference patterns.

The accompanying Figure shows a scanning electron micrograph (SEM) of a polymeric microstructure produced by exposure to the interference pattern
5 created at the intersection of four beams from a frequency-tripled injection seeded, Q-switched Nd:Yag laser of a 10 μ m film of photoresist based on Epon-SU8. The scale bar is 10 μ m. Refraction at the film surface changes the incident wavevectors, stretching the interference pattern in the [111] direction. During processing film shrinkage of 10-20% occurs. The developed film is hard and brittle; its top surface
10 is a (111) plane and it has been fractured to reveal (11 $\bar{1}$) cleavage planes.

CLAIMS

1. A method of forming a photonic crystal material comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation
5 whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3 with an equivalent weight per crosslinkable group of at most
10 1000.
2. A method according to claim 1, wherein the irradiated sample of photosensitive material is developed to remove less irradiated regions of the sample.
3. A method according to claim 1 or 2 wherein the photosensitive material is an epoxy resin.
- 15 4. A method according to any one of claims 1 to 3 wherein the number of crosslinkable groups per molecule is at least 6.
5. A method according to claim 4 wherein the number of crosslinkable groups per molecule is about 8.
6. A method according to any one of the preceding claims wherein the
20 equivalent weight per crosslinkable group is at most 300.
7. A method according to claim 6 wherein the equivalent weight per crosslinkable group is at most 230.
8. A method according to any one of the preceding claims wherein the photosensitive material is a glycidyl ether of bisphenol A novolac resin.
- 25 9. A method according to claim 8 wherein the resin is one where the number of epoxy groups per molecule is about 8 and the resin is co-polymerised with a less crosslinkable plasticising epoxy monomer.
10. A method according to any one of the preceding claims wherein the photosensitive material comprises a photoacid generator.
- 30 11. A method according to claim 10 wherein the photoacid generator possesses a molar extinction coefficient of 50 to 2000 mol⁻¹ dm³ cm⁻¹ at the

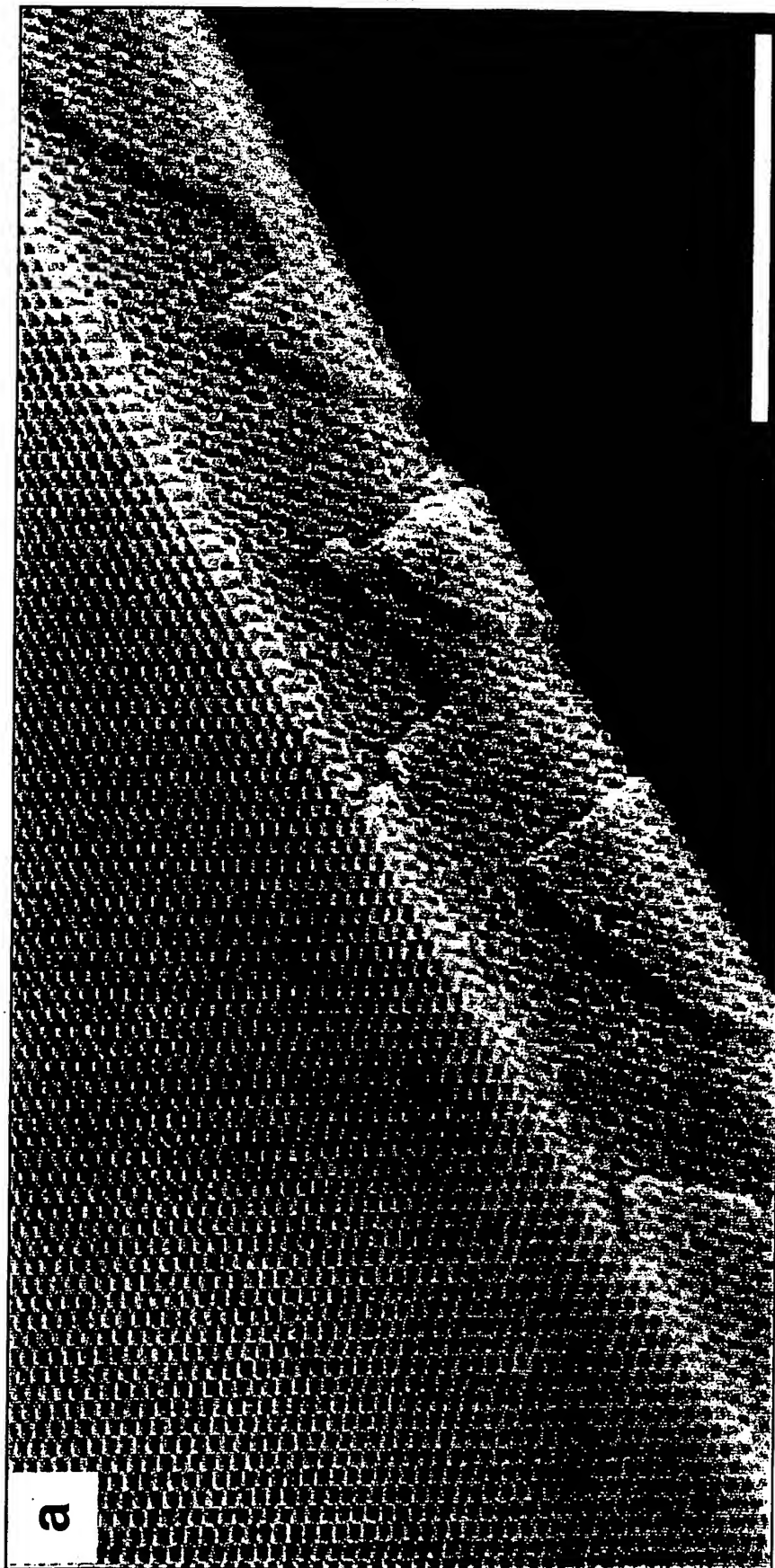
wavelength of radiation being used, is used at a concentration at which it does not absorb more than 5% of the radiation which is incident upon it while having a quantum efficiency which is sufficient for the exposure to cause insolubilisation of the photosensitive material.

- 5 12. A method according to claim 11 wherein the molar extinction coefficient is $100 \text{ to } 500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.
13. A method according to claim 11 or 12 wherein the photoacid generator is a triaryl sulphonium salt.
14. A method according to any one of the preceding claims wherein the
10 photosensitive material is cured by subsequent heating to cause acid catalysed polymerisation.
15. A method according to claim 14 wherein the photosensitive material is cured by heating at 40°C to 120°C for 1 to 20 minutes.
16. A method according to claim 14 or 15 wherein the heating is carried
15 out at a temperature below the melting point of the photosensitive material.
17. A method according to any one of the preceding claims wherein material is introduced into the voids produced by development of the irradiated photosensitive material.
18. A method according to claim 17 wherein the optical properties of the
20 irradiated sample are adjusted by the introduction of a material having a predetermined refractive index that is different from that of the irradiated photosensitive material.
19. A method according to claim 17 wherein the irradiated sample is used as a template for the production of other composite materials having periodic
25 variations in refractive index.
20. A method according to any one of the preceding claims, wherein the photosensitive material is subjected to multiple exposures, each exposure producing respective interference patterns.
21. A method according to any one of the preceding claims, wherein the
30 three dimensional pattern is formed by directing electromagnetic radiation from at least four beams at the photosensitive material so as to intersect and interfere within

it.

22. A method according to claim 1 substantially as hereinbefore described.

23. A photonic crystal material wherever formed by a method as claimed
5 in any one of the preceding claims.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03603

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G02B6/12 C08L63/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G02B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WITZGALL G ET AL: "Single-shot two-photon exposure of commercial photoresist for the production of three-dimensional structures" OPTICS LETTERS, 15 NOV. 1998, USA, vol. 23, no. 22, pages 1745-1747, XP000955303 ISSN: 0146-9592	1-3,8, 10-17, 22,23
Y	page 1745 page 1747, right-hand column --- -/--	4-7,9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

5 December 2000

Date of mailing of the international search report

21/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

von Moers, F

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/03603

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	LEE K Y ET AL: "Micromachining applications of a high resolution ultrathick photoresist" JOURNAL OF VACUUM SCIENCE & TECHNOLOGY B , NOV.-DEC. 1995, USA, vol. 13, no. 6, pages 3012-3016, XP002154618 ISSN: 0734-211X page 3012	4-7,9
X	WO 99 09439 A (DENNING ROBERT GORDON ;TURBERFIELD ANDREW JONATHAN (GB); ISIS INNO) 25 February 1999 (1999-02-25) cited in the application	23
A	page 10, line 15 -page 15, line 30	1,18-21
P,X	CAMPBELL M ET AL: "Fabrication of photonic crystals for the visible spectrum by holographic lithography" NATURE, 2 MARCH 2000, MACMILLAN MAGAZINES, UK, vol. 404, no. 6773, pages 53-56, XP000961267 ISSN: 0028-0836 the whole document	1-23

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 00/03603

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9909439 A	25-02-1999	EP 1005661 A	07-06-2000